

AD-774 126

MOLECULAR BEAM EPITAXY OF II-VI
COMPOUND WAVEGUIDES

Donald L. Smith

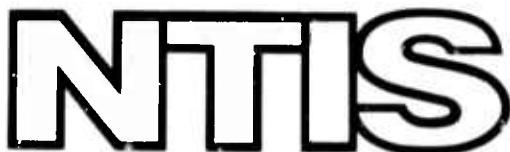
Perkin-Elmer Corporation

Prepared for:

Advanced Research Projects Agency
Office of Naval Research

31 December 1973

DISTRIBUTED BY:



National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

AD774126

PERKIN-ELMER

AD774126

31 December 1973

QUARTERLY TECHNICAL REPORT

1 October through 31 December 1973

ARPA Order No. 2327

Contract No. N00014 73-C-0280

Program Code No. 3D10

Principal Investigator:
Dr. Donald L. Smith
203-762-6916

Contractor:
Perkin-Elmer Corporation

Scientific Officer:
Director, Naval Research Laboratory

Effective Date of Contract:
1 March 1973
(received 28 June 1973)

Title: Molecular Beam Epitaxy of
II-VI Compound Waveguides

Contract Expiration Date:
28 February 1974

Amount of Contract: \$50,000.00

The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the Advanced Research Projects Agency or the U.S. Government

Sponsored by

Advanced Research Project Agency

ARPA Order No. 2327

1.

15-

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER <i>AD774 126</i>
4. TITLE (and Subtitle) MOLECULAR BEAM EPITAXY OF II-VI COMPOUND WAVEGUIDES		5. TYPE OF REPORT & PERIOD COVERED Quarterly Report 1 Oct. through 31 Dec. 73
7. AUTHOR(s) Dr. Donald L. Smith		6. PERFORMING ORG. REPORT NUMBER 11821 8. CONTRACT OR GRANT NUMBER(s) N0014-73-C-0280
9. PERFORMING ORGANIZATION NAME AND ADDRESS Perkin-Elmer Corporation 50 Danbury Road Wilton, Conn. 06897		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Advanced Research Projects Agency		12. REPORT DATE 21 January, 1974
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Office of Naval Research		13. NUMBER OF PAGES 15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
17. DISTRIBUTION STATEMENT (for the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) epitaxy; vacuum evaporation; optical waveguides; II-VI semiconductors		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) > II-VI compound optical waveguide growth is being studied experimentally using molecular beam epitaxy, a closely-controlled form of vacuum evaporation, under ultra-high vacuum. The objective is to generate low-loss single-crystal guides suitable for constructing active elements in optical communications systems. " " "		

20.

Upper limits to growth temperature, upon which crystal quality is critically dependent, have been established for CdSe and ZnTe and have been found due in the former case to element volatilities and in the latter case to compound decomposition. Waveguides in ZnSe and ZnTe have been demonstrated at 0.633 microns using both prisms and tapered edges to couple the light, and coupling angles agree exactly with values predicted from measured film parameters. Chemical polishing techniques for CdS and CdSe substrates have been developed.

The effect of growth temperature will be studied further using a quartz-crystal monitor. Waveguiding measurements will be made in both the visible and the infrared on several binary and ternary II-VI films.

iii.

TABLE OF CONTENTS

I.	SUMMARY-----	page 1
II.	TECHNICAL DISCUSSION	
A.	FILM GROWTH KINETICS-----	page 2
B.	SUBSTRATE PREPARATION-----	page 4
C.	WAVEGUIDE MEASUREMENTS-----	page 5
III.	PROGRAM PLANS-----	page 7
TABLE I-----		page 8
FIGURES-----		page 9
REFERENCES-----		page 10

I. SUMMARY

II-VI compound optical waveguide growth is being studied experimentally using molecular beam epitaxy, a closely-controlled form of vacuum evaporation, under ultra-high vacuum. The objective is to generate low-loss single-crystal guides suitable for constructing active elements in optical communications systems.

Upper limits to growth temperature, upon which crystal quality is critically dependent, have been established for CdSe and ZnTe and have been found due in the former case to element volatilities and in the latter case to compound decomposition. Waveguides in ZnSe and ZnTe have been demonstrated at 0.633 microns using both prisms and tapered edges to couple the light, and coupling angles agree exactly with values predicted from measured film parameters. Chemical polishing techniques for CdS and CdSe substrates have been developed.

The effect of growth temperature will be studied further using a quartz-crystal monitor. Waveguiding measurements will be made in both the visible and the infrared on several binary and ternary II-VI films.

A. FILM GROWTH KINETICS

We have made careful measurements of impingement rates of constituent elements and of film growth rates for several II-VI compounds at various substrate temperatures in order to elucidate the growth kinetics. The Zn and Te_2 impingement rate calibrations made last quarter on room-temperature glass have been repeated on LN_2 -cooled Cu Substrates with deposit mass measurement by atomic absorption spectrophotometry as well as thickness measurement by interference microscopy. This experiment revealed that while the sticking coefficient S of Zn at 23°C is unity as had been assumed, that of Te_2 is only $2/3$. For Cd on 23°C sapphire, S=0. Since the evaporation rates of these elements are not significant until well above 23°C (see Table I), compared to calculated impingement rates which were equivalent to 1 micron/hr, the above result suggests that the impinging Te_2 and Cd is being reflected from the substrate rather than condensing and then evaporating.

For compound growth from elemental sources at impingement rates equivalent to 1 micron/hr, it has been found that S=1 for growth on CaF_2 , sapphire, and CdS of ZnSe at 300°C and ZnTe at 350°C . For ZnTe on 450°C sapphire, S=0 on the clean substrate, but S= $2/3$ if growth is first initiated at 350°C . For CdSe on CaF_2 , S= $1/10$ at 250°C and S=0 at 350°C . Several interesting conclusions may be drawn from these results. Since the compounds may be grown at temperatures far above those at which the individual

elements would be expected to cease condensing and since S is greater for ZnTe on ZnTe than on other surfaces, impinging atoms must be reacting with the surface to form a II-VI bond immediately upon approach, rather than condensing first. For ZnTe, this process occurs with S=1 right up to the compound decomposition temperature (see Table I). On the other hand, CdSe ceases to deposit well below this temperature. Since Cd and Se are both more volatile than Zn and Te, this result suggests that both the elemental volatilities and the compound decomposition temperature have an effect on the maximum growth temperature. Similarly, Ford researchers have found that Hg volatility limits $(\text{HgCd})\text{Te}$ growth temperature to 150°C^4 . This is a complicated situation which warrants further study.

B. SUBSTRATE PREPARATION

The bromine/methanol-polished CdSe substrates prepared last quarter had appeared featureless by conventional microscopy and had given good low-energy electron diffraction (LEED) patterns after ion-bombardment cleaning, but have now been found to be scratched when examined by Nomarski microscopy. A NaOCl/silica polish does give featureless surfaces which are now being examined by LEED.

A polishing mixture of $\text{HNO}_3/\text{AlCl}_3/\text{silica}$ developed this quarter has generated CdS(0001A) surfaces which are completely featureless under 400X Nomarski examination and which give good LEED patterns (see Figure 1) after a 1-minute heat-cleaning at 450°C , without the need for the usual³ ion-bombardment. Auger spectroscopy has shown only 1/10 monolayer of residual contamination (C and Cl). This work is being submitted for publication.

C. WAVEGUIDE MEASUREMENTS

Waveguiding at 0.633 microns has been observed this quarter in ZnTe films using a taper coupler and in ZnSe films using a prism coupler. Films with edges tapered smoothly to zero thickness over a distance of about 0.3 mm (see Figure 2) have been grown by employing a knife-edge mask spaced about 5 mm from the substrate and aligned parallel to the Zn and Te₂ effusion cells, so that a diffuse shadow of the cell orifices is cast on the substrate. Light is focused on the couplers through the polished edges of the CaF₂ substrates. A streak about 5 mm long has been observed in a 1-micron thick film of ZnTe.

ZnSe guides have been achieved using a clamped-on rutile prism. A 2 mm streak was observed in a 1.7 micron film on sapphire which the vendor had supplied 30° off the desired (0001) orientation. This film was undoubtedly polycrystalline. Seven modes, with the lowest mode having a 5 mm-long streak, have been observed in a ZnSe film on CaF₂ (111). From coupling angle measurements we have calculated the film's bulk index of refraction to be 2.58 and its thickness to be 1.62 microns, agreeing exactly with the known ZnSe index of 2.58 at 0.633 microns and the interferometrically-measured film thickness of 1.6 microns.

ZnTe films were grown on CdS before the polishing technique was perfected, but they did not exhibit waveguiding. They were, however, mirror-smooth and extremely adherent, able to be washed with det-

ergent-soaked cotton swabs without damage, indicating absence of thermal strain and good chemical bonding to the substrate.

III. PROGRAM PLANS

A quartz-crystal thickness monitor specially designed to operate at 200-500°C is being installed to expedite measurements of sticking coefficient as a function of substrate temperature and growth rate for all four of the II-VI compounds. This data is expected to be of great value in optimizing growth conditions.

In a parallel effort, various binary and ternary II-VI compounds will be grown on CdS(0001) and CdSe(0001) substrates, and waveguiding measurements will be made using prism and/or taper couplers.

TABLE I

Approximate Temperatures for
Evaporation Rates of
1 micron/hr (1 monolayer/sec.)

elements ¹	°C	compounds ²	°C
Se	110	CdTe	410
Cd	120	ZnTe	470
Zn	180	CdSe	480
Te	230	ZnSe	560

9.

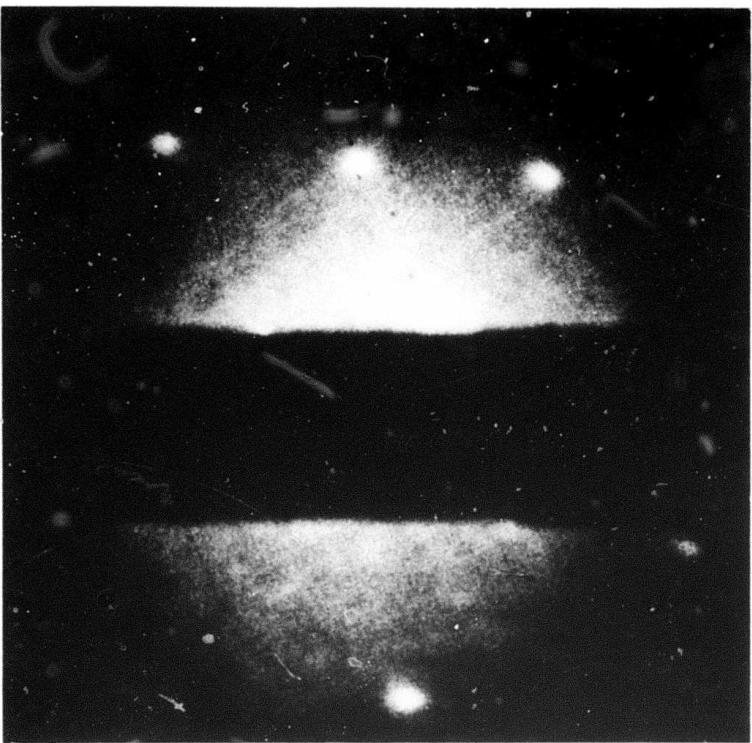
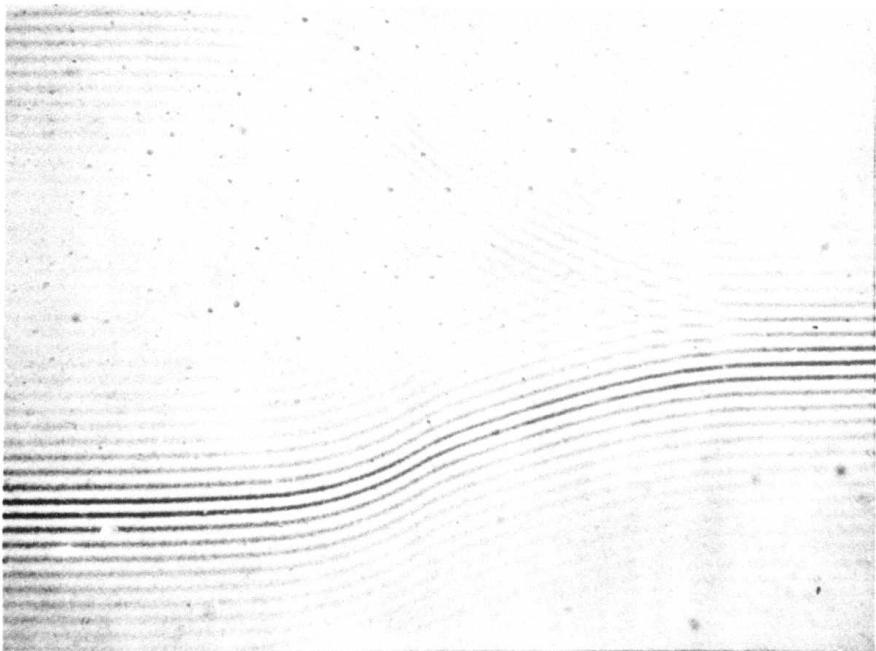


Figure 1. LEED Pattern of CdS(0001A) at 92eV



↔ 0.1 mm. →

Figure 2. Interference Micrograph of Tapered Edge of ZnTe Film on CaF_2 . Film is to right, substrate to left. One fringe = $0.3\mu\text{m}$.

REFERENCES

1. R. E. Honig + D. A. Kramer; RCA Review 30 285 (1969)
2. P. Goldfinger + M. Jeunehomme; Trans. Faraday Soc. 59 2851
3. B. D. Campbell and H. E. Farnsworth; Surf. Sci. 10, 197 (1968)
4. D. K. Hohnke, H. Holloway, E. M. Logothetis, and R. C. Crawley;
J. App. Phys. 42, 2487 (1971)